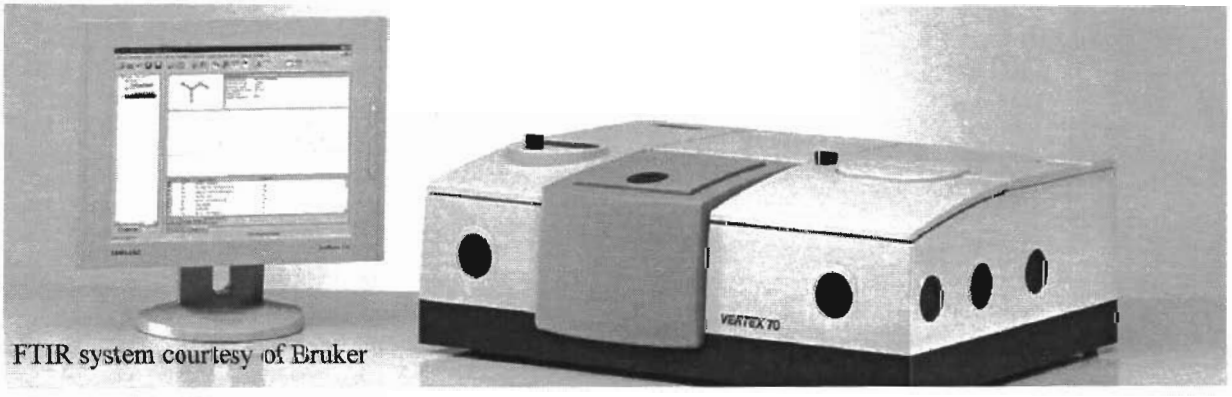
Training Manual
Product 5-9028-01-P1
Project 5-9028-01

Application of FTIR for Lime Analysis

S. Nasrazadani and
E. Eureste

Engineering Technology Department
University of North Texas
Denton Texas 76207

April 2008



FTIR system courtesy of Bruker

Technical Report Documentation Page

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
FHWA/TX-08/5-9028-01-P1		

4. Title and Subtitle	5. Report Date
Application of FTIR for Quantitative Analysis of Lime	April 16, 2008
	6. Performing Organization Code

7. Author(s)	8. Performing Organization Report No.
Seifollah Nasrazadani and Esteban Eureste	5-9028-01-P1

9. Performing Organization Name and Address	10. Work Unit No. (TRAIS)
University of North Texas 3940 N. Elm- Suite F115X (Research Park) Denton Texas 76207	11. Contract or Grant No. 5-9028-01

12. Sponsoring Agency Name and Address	13. Type of Report and Period Covered
Texas Department of Transportation Research and Technology Implementation Office P.O. Box 5080 Austin, TX 78763-5080	Training Manual March 2007-February 2008
	14. Sponsoring Agency Code

15. Supplementary Notes
Project performed in cooperation with the Texas Department of Transportation and the Federal Highway Administration.

16. Abstract

TxDOT currently uses the titration method for the quantitative analysis of lime samples. The titration method is time consuming (hours if not an entire day is spent for each analysis) and it is not an accurate test due to chemical interferences and sample preparation variances. In addition, the titration method consumes chemicals that are costly and add to hazardous waste inventory. On the other hand, lime and its related materials absorb Infrared rays and exhibit their fingerprint spectra that are free of spectral interferences. In this implementation project, application of Fourier Transform Infrared spectroscopy (FTIR) was investigated for rapid and accurate quantitative analysis of lime from three forms including quick lime, hydrated lime and slurry lime. Calibration curves relating absorption relative intensities of lime to lime concentrations (for both quicklime and slurry lime samples) were generated that showed $R^2 = 0.88$, and will be utilized to quantify lime content of an unknown sample. Sample preparation method for different forms of lime is discussed and precautions to consider for interference avoidance are discussed. Results indicated that FTIR is a safe and straightforward method that requires minimal operator training and expertise. Finally, a testing protocol for lime quantification using FTIR was developed.

17. Key Word	18. Distribution Statement
FTIR, lime analysis, quick lime, hydrated lime, slurry lime	No restrictions. This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161, www.ntis.gov.

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
unclassified		16	

Deliverable: Training Manual

Researchers: Dr. Seifollah Nasrazadani, Esteban Eureste, University of North Texas

Deliverable Number: P1 of Project Number 5-9028-01

Project Number: 5-9028-01

Project Title: Application of FTIR for Quantitative Lime Analysis

Sponsoring Agency: Performed in cooperation with the Texas Department of Transportation and the Federal Highway Administration

Date: 4/15/08

Performing Agency: University of North Texas (Performed in cooperation with Texas Department of Transportation and the Federal Highway Administration)

Disclaimers

Author's Disclaimer: The contents of this report reflect the views of the author(s), who is (are) responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official view or policies of the Federal Highway Administration (FHWA) or the Texas Department of Transportation (TxDOT). This report does not constitute a standard, specification, or regulation.

Engineering Disclaimer: This report is not intended for construction, bidding, or permit purposes.

Manufacturers' Notice: The Unites States Government and the State of Texas do not endorse products or manufacturers. Trade or manufacturers' names appear herein solely because they are considered essential to the object of this report.

1.0 Introduction:

Quality of lime is determined based on available CaO in quicklime or $Ca(OH)_2$ in hydrated (slurry) lime. In either case the primary factor that determines the quality is the percentage of available lime which is the actual chemical "lime" either as CaO or $Ca(OH)_2$, though usually quoted in terms of the equivalent CaO content. Pure quicklime will have 100% available CaO, whilst pure hydrated lime, $Ca(OH)_2$, will contain 75.56 available CaO.

1.1 Basics of Fourier Transform Infrared Spectroscopy (FTIR):

Fourier Transform Infrared Spectroscopy is a well-established analytical technique used for analysis of solids, liquids and gases. This technique is routinely used for research and development, as well as quality control/quality assurance in many industries including pharmaceutical, paper and pulp, and polymers and plastics. FTIR was primarily developed for analysis of organic matters based on their chemical bonding characteristics, but more and more, this technique is finding its applications in the analysis of inorganic matters like oxides, nitrides, etc. Relatively weaker chemical bonds in organic matters excite easier than stronger bonds between a metallic element like iron and oxygen; however, chemical bonding in many oxides including CaO and oxide-hydroxide such as $Ca(OH)_2$ are weak enough to generate a vibration spectrum that could be used for analytical purposes. The fact that lime and its derivatives produce an interferometer spectrum will be utilized in this project to quantitatively analyze lime samples.

1.1.1 Working Principle: FTIR involves the twisting, rotating, bending, and vibration of the chemical bonding (Figure 1). Let incident infrared radiation intensity be I_o and I be the intensity of the beam after it interacts with the sample. The ratio of intensities I/I_o as a function of frequency of light gives a spectrum, which can be in three formats: as transmittance, reflectance, and absorbance. The multiplicity of vibrations occurring simultaneously produces a highly complex absorption spectrum, which is a unique

characteristic of the functional groups comprising the molecule, and also the configuration of the atoms. A detector is used to read out the intensity of light after it interacts with the sample. The typical setup of a FTIR is as shown in the Figure 2. The author has successfully applied this technique for the identification and characterization of iron oxides [3-6]. Specifically, magnetite and maghemite that are not differentiable with popular x-ray diffraction technique were successfully identified by FTIR [5].

Advantages of applying this technique for quantification of lime include:

- Minimal sample preparation
- Fast, reliable, and robust analysis
- No need of messy chemicals
- No spectra interferences
- Fully computerized analysis
- Ease of operation and minimal operator training and expertise

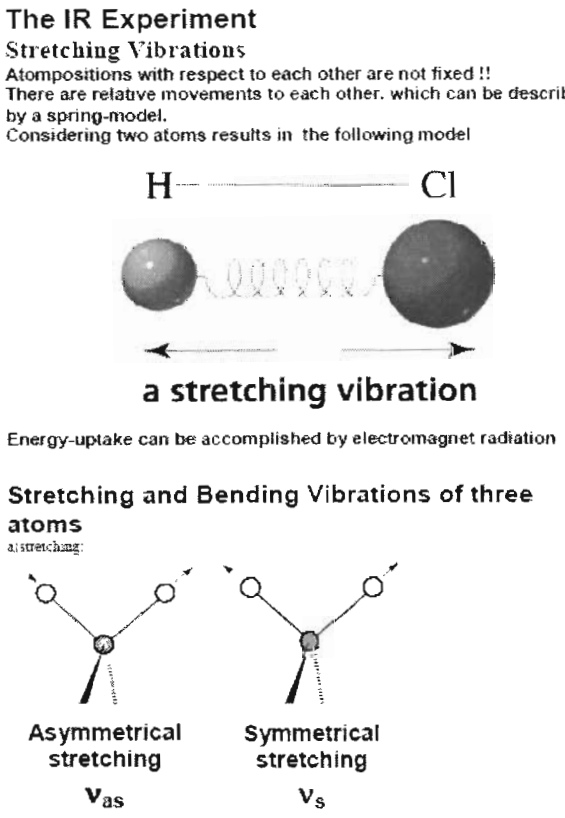


Figure 1: Stretching and bending vibrations of atoms due to absorption of IR radiation.

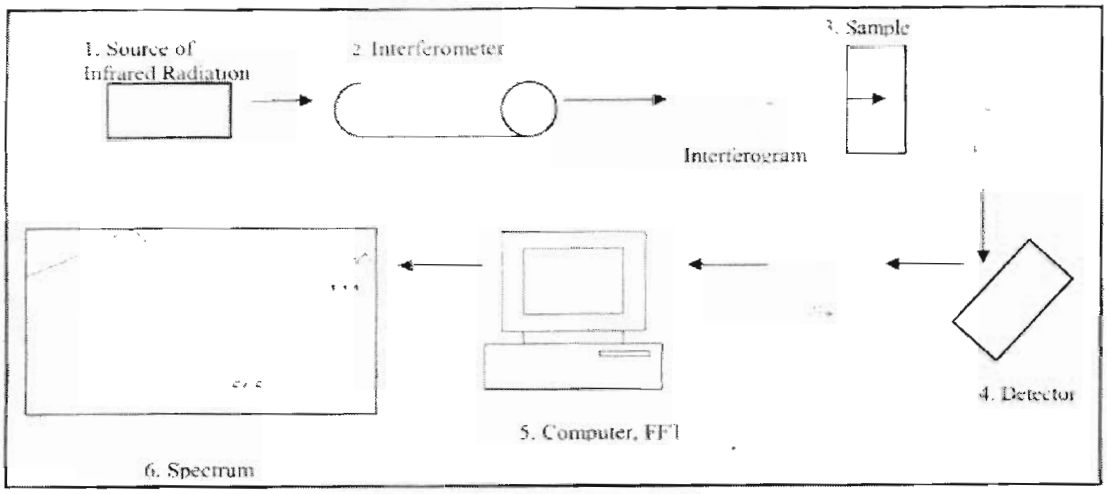


Figure 2. Experimental set-up for Fourier Transform Infrared Spectroscopy
(Adapted from Richard Brundle et al, 1992)

2.0 Lime Quantification Procedure:

2.1 Sample Preparation

2.1.1 Required Equipment

- Pestle and Mortar Set
- Digital Scale (precision >0.1 mg)
- Hydraulic Press Capable of >12k psi
- 13 mm Pellet Die Set with Vacuum Attachn
- Vacuum Pump with a Compatible Pellet Die Connection
- IR pellet Sample Holder Cards
- Tweezers
- Weighting Papers

Required Chemicals

- IR Grade Potassium Bromide

- Reagent Grade Potassium Ferricyanide

1. Prepare a mixture of 2 mg of sample, 2 mg of Potassium Ferricyanide, and 100 mg of Potassium Bromide.

2. Grind the mixture for approximately 3 minuets with a pestle in a mortar, so that the mixture is a uniform fine powder. It is highly recommended that the pestle and mortar set be kept in an oven when not in use to keep moisture from accumulating. It is also important that the set is at room temperature when used.

3. Then deposit the mixture in a 13 mm pellet die. By hand lightly tap the die to spread the mixture as evenly as possible across the bottom anvil, then insert the plunger and slowly rotate it 1-1.5 turns making sure not to apply pressure. Then remove plunger and proceed with the top anvil and compress with the plunger. Compress the mixture with 12k psi for 4 minuets under vacuum. As with the grinding set the die should be kept in an oven when not in use, but should be allowed to cool to room temperature before use.

4. Carefully remove the pellet from the die with tweezers and place the pellet in an IR pellet sample holder card. Often the sample is not fully uniformly compressed, so white spots may appear, in which case avoid placing the white spot in the center of the holder window.

2.2 Cautions: Pay Attention to Interfering Factors

Several experiments were performed to identify what factors affected the results of FTIR test. Some of the factors that were experimented with were compression strength, sample sizes, atmosphere exposure, and type of FTIR test (transmission or

reflection). Figure 3 shows how the variation in compression strength affects the FTIR spectra, the variation demonstrates an inconsistent peak profile. Another factor that was identified from the literature review as a potential factor was exposure to humidity in the atmosphere. Time trials were performed that exposed samples to the atmosphere, Figure 4 shows the profiles of samples exposed to the atmosphere for different amounts of time. Sample sizes are also important; too much sample in the pellet could lead to peaks that max out the FTIR scale for absorbance. It was also determined that transmission is superior to reflectance test for quantitative purposes. With these factors in mind a protocol was developed which will maximize repeatability, precision, and accuracy.

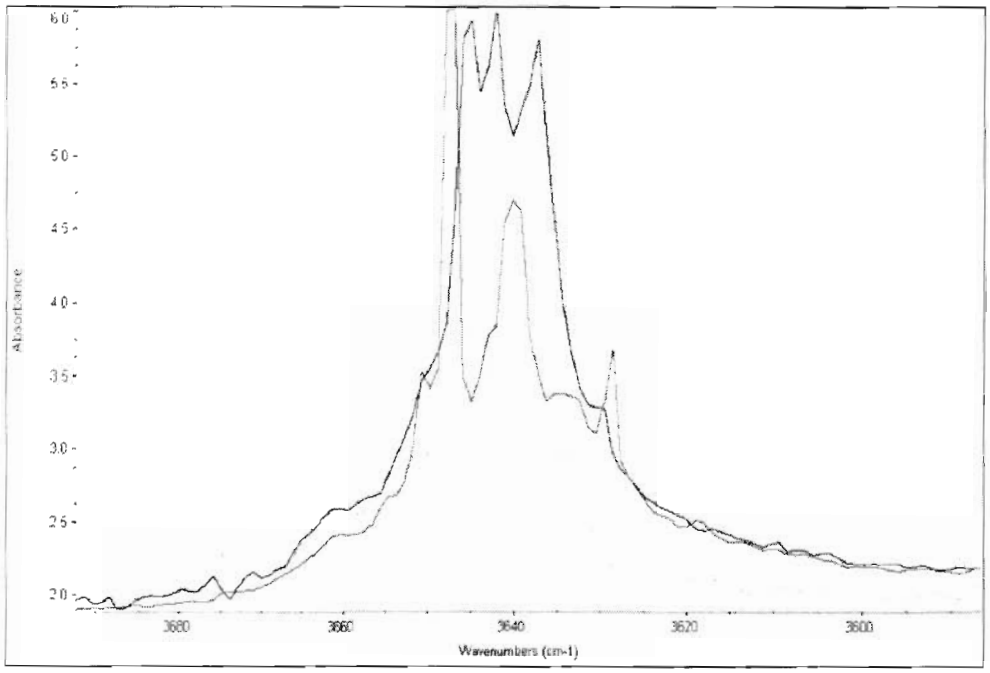


Figure 3: Variation in Pressure in Pellet Die.
Light Blue-5kpsi; Dark Blue-10kpsi; Red-15kpsi

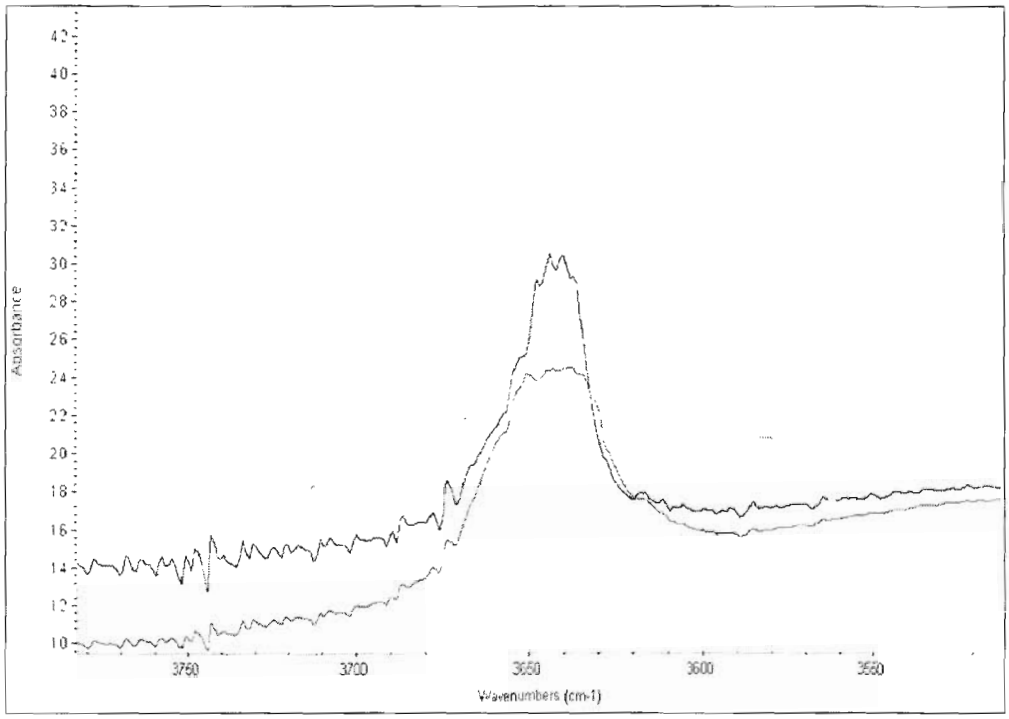


Figure 4: Variation in Atmosphere Exposure.
Green-24hrs; Blue-48 hrs; Red-72 hrs

2.3 Steps involved in the analysis:

1. Prepare sample using KBr method.

2. Collect FTIR spectrum (4000-400 cm^{-1}) for background (Figure 5) and the sample.

3. Subtract background spectrum (Figure 5) from that of the sample to get what is shown in Figure 6.

4. Identify absorption bands of lime and impurities.

5. Measure intensity of several known concentration.

6. Draw calibration curve for lime analysis Figures 7 and 8 for quicklime and slurry lime samples respectively.

7. Measure absorption band intensity of an unknown sample containing lime.

8. Calculate lime concentration.

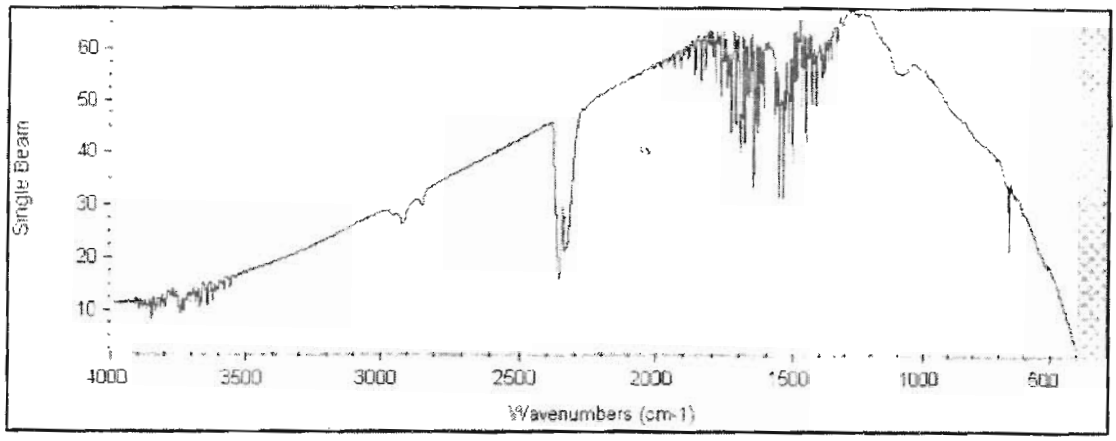


Figure 5: FTIR spectrum of laboratory air that is considered as background.

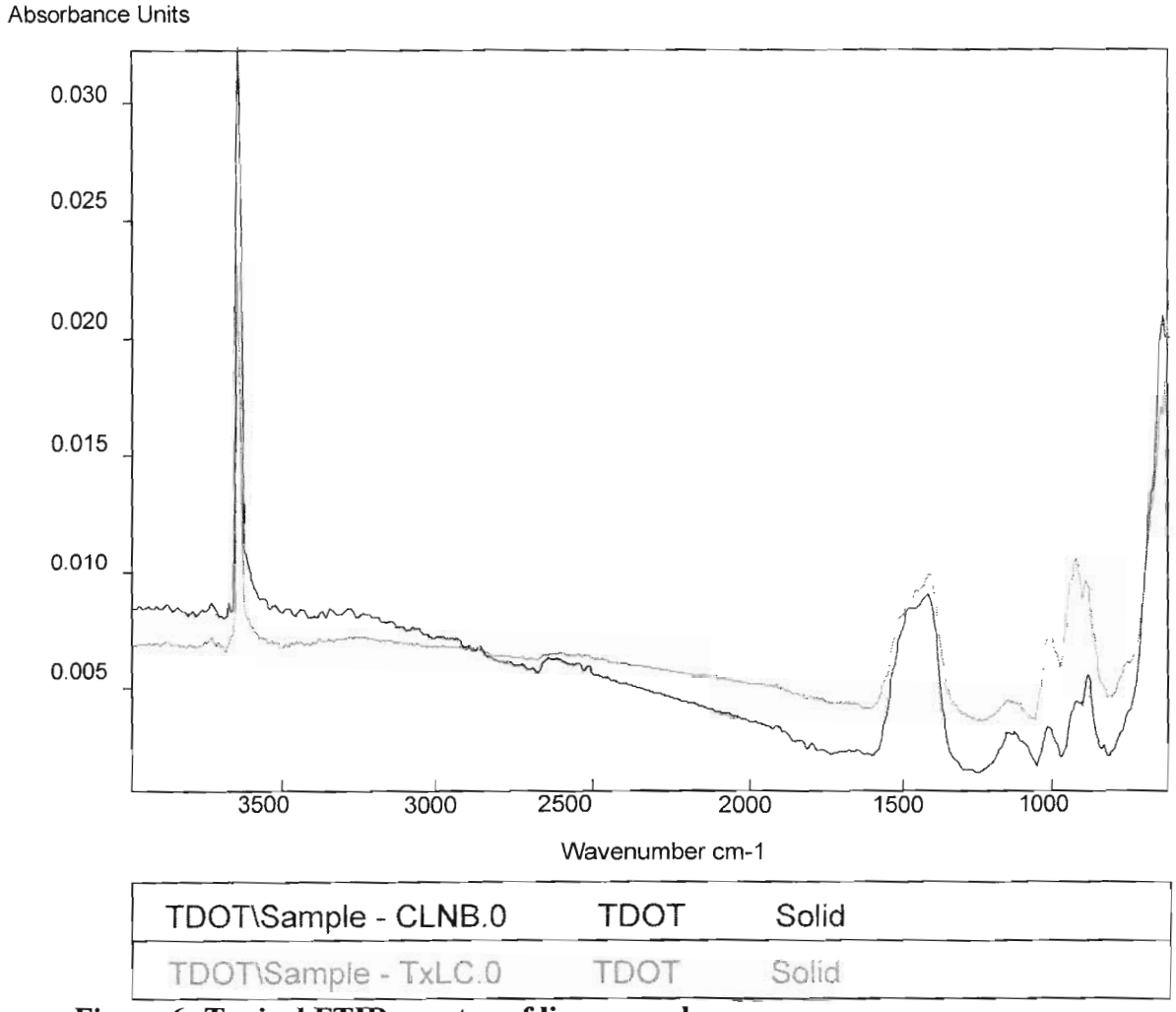


Figure 6: Typical FTIR spectra of lime samples.

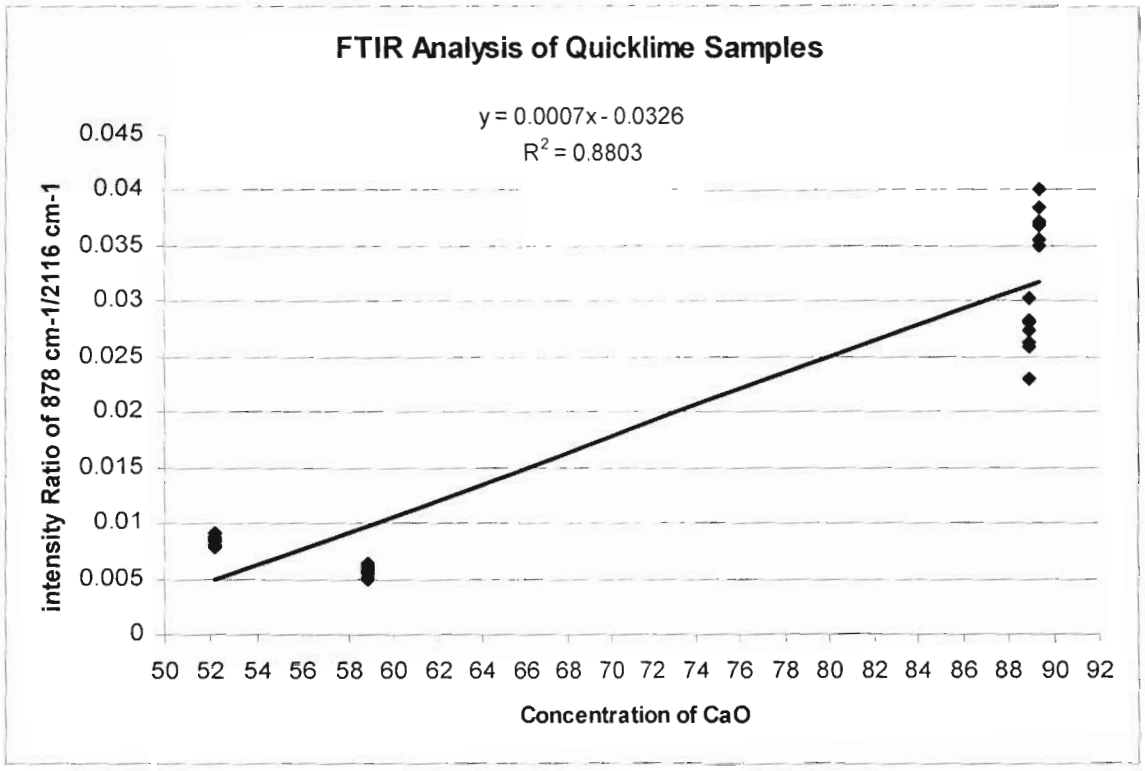


Figure 7: Calibration curve for quicklime samples.

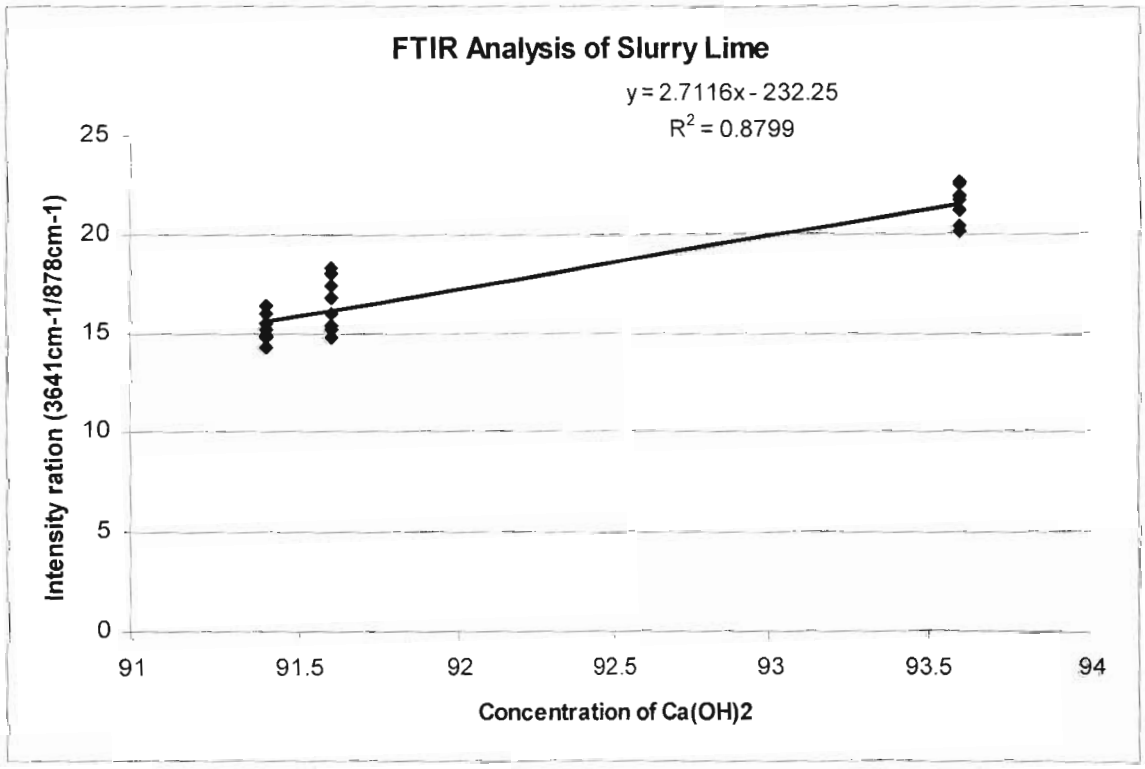


Figure 8: Calibration curve for hydrated (slurry) lime samples.

2.4 Sample calculations:

An unknown sample of quicklime shows relative intensity of 878 cm^{-1} /2116 cm^{-1} absorption ratio of 0.03. The actual lime concentration in this sample is about 88 % using Figure 7. Note standard reference used in this case was potassium ferricyanide that show FTIR absorption band at 2116 cm^{-1} and absorption band for CaO was taken at 878 cm^{-1}. One could obtain the same result by calculation as shown below.

$$Y=0.0007\ X - 0.0326$$

In this case Y= intensity ratio and X represent the CaO concentration.

$$X=(Y+0.0326)/\ 0.0007$$

$$X=(0.03+0.0326)/\ 0.0007 = 89\%$$

About 1% deviation between the graphical and mathematical methods is due to the correlation factor $R^2 = 0.88$.

Similar analysis can be done for hydrated (slurry) lime using Figure 8.